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Magnetic properties of Aurivillius lanthanide-bismuth $(LnFeO_3)_nBi_4Ti_3O_{12}$ (n = 1,2) layered titanates

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Bismuth titanates of Aurivillius layer-structure $(BiFeO_3)_nBi_4Ti_3O_{12}$, are of great technological interest because of their applications as non-volatile ferroelectric memories and high-temperature piezoelectric materials. The synthesis and crystallographic characterization of a new family of compounds $(LnFeO_3)_nBi_4Ti_3O_{12}$ was recently reported, in which the layers consist of $LnFeO_3$ perovskites with a lanthanide Ln^{3+} substituting diamagnetic Bi^{3+}.
We report herein the magnetic properties of bulk samples, with Ln = Nd, Eu, Gd and Tb, and n = 1 and 2. Single-layer materials are paramagnetic, similar to non-substituted bismuth titanate $Bi_5FeTi_3O_{15}$, and show crystal field effects due to the crystallographic environment of Eu^{3+} and Tb^{3+}. Several anomalies are detected in the magnetization M(T) of double-layer $(LnFeO_3)_2Bi_4Ti_3O_{12}$ compounds, related to the strong magnetism of Tb and Gd, since they weakly appear for Nd and they are absent in the VanVleck Eu^{3+} ion and in the parent $Bi_6Fe_2Ti_3O_{18}$ compound.

Keywords: multiferroic materials, superexchange interactions, lanthanide perovskites, Aurivillius structure

Propiedades magnéticas de titanatos laminares de lantánido-bismuto, con estructura tipo Aurivillius, $(LnFeO_3)_nBi_4Ti_3O_{12}$ (n = 1,2)

Los titanatos de hierro y bismuto con estructura laminar tipo Aurivillius, $(BiFeO_3)_nBi_4Ti_3O_{12}$, tienen un gran interés tecnológico debido a sus aplicaciones como memorias ferroeléctricas no volátiles y como piezoeléctrico cerámico de alta temperatura. La síntesis y la caracterización cristalina de una nueva familia de compuestos $(LnFeO_3)_nBi_4Ti_3O_{12}$ han sido recientemente reportadas, en la que el catión diamagnético Bi^{3+} ha sido sustituido por los paramagnéticos Ln^{3+} en los bloques de perovskita.
Se estudian las propiedades magnéticas de muestras cerámicas en volumen con Ln = Nd, Eu, Gd y Tb, y n = 1 y 2. Los materiales con n=1 son paramagnéticos y similares al no sustituido $Bi_5FeTi_3O_{15}$, y muestran efectos de campo cristalino debido al entorno cristalino de Eu^{3+} y Tb^{3+}. Se han detectado algunas anomalías en la magnetización M(T) de los compuestos n=2 $(LnFeO_3)_2Bi_4Ti_3O_{12}$ que están relacionadas con el fuerte magnetismo de Tb y Gd, que aparecen débilmente para Nd y que no aparecen para el ión VanVleck Eu^{3+} ni en el compuesto pariente $Bi_6Fe_2Ti_3O_{18}$.

Palabras clave: materiales multiferroicos, interacciones de supercanje, perovskitas con lantánidos, estructura Aurivillius.

1. INTRODUCTION

Bismuth layered titanates $(BiFeO_3)_nBi_4Ti_3O_{12}$ of the well-known Aurivillius structure are interesting materials for technological applications such as non-volatile ferroelectric memories and high-temperature piezoelectricity (1,2). Because of the presence of ferroelectric and magnetoelectrical transitions they may be considered as potential multiferroic materials in which magnetic and ferroelectric order may coexist (3-6). The magnetic and magneto-electrical properties are governed by superexchange interactions between Fe^{3+} cations and as such, it becomes interesting to modulate the number of layers, the interlayer distance and to insert other magnetic ions in order to promote intra and interlayer magnetic interactions. One way to modulate such properties is to substitute diamagnetic Bi^{3+} by a magnetic lanthanide Ln^{3+} as, for instance, heavy lanthanides of large magnetic moment or lighter elements in which crystal field effects are predominant. We have recently reported the synthesis and crystallographic characterization of such new family of compounds $(LnFeO_3)_nBi_4Ti_3O_{12}$, in which the layers consist of $LnFeO_3$ perovskites, the number of layers being kept to n = 1 and 2 (7). In this work, we complete their characterization, by reporting the magnetic properties for Ln = Tb, Eu, Gd and Nd.

2. EXPERIMENTAL PROCEDURE

The compounds were prepared by solid-state reaction from submicronic powders of the corresponding oxides. The synthesis was carried out at 1000 - 1050 ºC. X-ray powder diffraction analysis of the synthesized compounds showed a crystalline structure isomorphous with that of the $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$. The sintering behaviour was characterized by

dilatometric measurements. The microstructure was observed by Scanning Electron Microscopy. All crystallochemical, structural and microstructural results are published elsewhere (7).

Magnetic properties were measured on a MPMS XL5 Quantum Design SQUID magnetometer on the range [5 K- 400 K] and, when necessary, using the furnace option up to 800 K. An applied field of 1 kOe was used to measure the magnetic susceptibility below 400 K, while 10 kOe was preferred for the high temperature measurements. Magnetization as a function of field was also performed at T = 5 K.

Lanthanide-free Aurivillius phases, i.e., $(BiFeO_3)_n(Bi_4Ti_3O_{12})$, n = 1 and 2, were also studied as "blank" samples and they allowed to isolate the effect of the magnetic rare-earths inserted in between the $Bi_4Ti_3O_{12}$ layers. Supplementary data were also obtained for ceramic samples of $BiFeO_3$.

3. RESULTS

The lanthanide-free compounds $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$ show paramagnetic properties, in contrast with reports about an antiferromagnetic state with Néel temperatures of 80 K and 160 K, for n=1 and n=2, respectively (8); their high-temperature behaviour was analyzed in terms of a Pauli-type temperature-independent paramagnetic susceptibility (χ_{TIP}), of the order of 4.5×10^{-3} and 11×10^{-3} emu/mol, respectively (7). Data on the starting compounds were then subtracted from the total signal of the isostructural lanthanide-containing series, thus leaving solely the effect of the lanthanide ion. This procedure was done for the single-layer $(LnFeO_3)(Bi_4Ti_3O_{12})$ (Ln = Eu and Tb) and double-layer $(LnFeO_3)_2(Bi_4Ti_3O_{12})$, (Ln = Nd, Eu, Gd and Tb).

3.1. Single layer series $(LnFeO_3)(Bi_4Ti_3O_{12})$ = $LnFeBi_4Ti_3O_{15}$

Figure 1 shows the temperature dependence of the magnetic susceptibility of the single layer compound $EuFeBi_4Ti_3O_{15}$, together with the magnetic contribution of the lanthanide-free $Bi_5FeTi_3O_{15}$ matrix. The difference between both curves χ_{diff}, related to the magnetic behaviour of the Eu ion, is also plotted at the bottom of figure 1. The reciprocal value $1/\chi_{diff}$ of their difference (insert) yields an effective moment of about 5.35 μ_B, which we attribute to the admixture between the $^7F_0$ and the $^7F_1$ multiplets of the VanVleck Eu^{3+} ion (9).

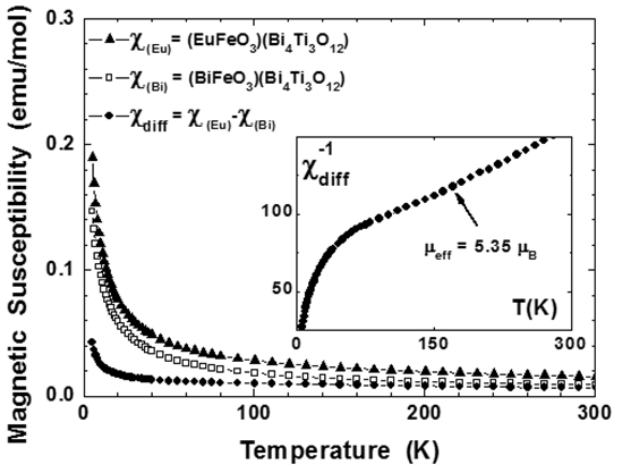

Fig. 1- Magnetic susceptibility of $EuFeBi_4Ti_3O_{15}$ (filled triangles) and $Bi_5FeTi_3O_{15}$ (open squares), and their difference χ_{diff} (filled circles). Insert shows the inverse susceptibility of the calculated difference. Susceptibilidad magnética de $EuFeBi_4Ti_3O_{15}$, (triángulos llenos) y de $Bi_5FeTi_3O_{15}$ (cuadrados abiertos), y su diferencia, χ_{diff} (círculos llenos). Los insertos muestran los valores $1/\chi_{diff}$.

The magnetization ZFC/FC cycle (at 50 Oe) for $TbFeBi_4Ti_3O_{15}$ is shown in figure 2, together with the inverse susceptibility (at 1 kOe) before and after subtraction of the $Bi_5FeTi_3O_{15}$ contribution (insert). The effective moment (9.79 ± 0.05 μ_B) is very close to the expected value for non-interacting Tb^{3+} ions (9.72 μ_B). No magnetic interactions Fe-Fe, Fe-Tb or Tb-Tb were then observed, as confirmed by the low Curie-Weiss temperature Θ = - 6 ± 0.5 K. On the other hand, the "saturation" moment for Tb (5.5 μ_B at 50 kOe and 5 K; not shown), much lower than the expected value $gJ(Tb^{3+}) = 9\ \mu_B$, indicates that crystal field effects are quite important at low temperatures.

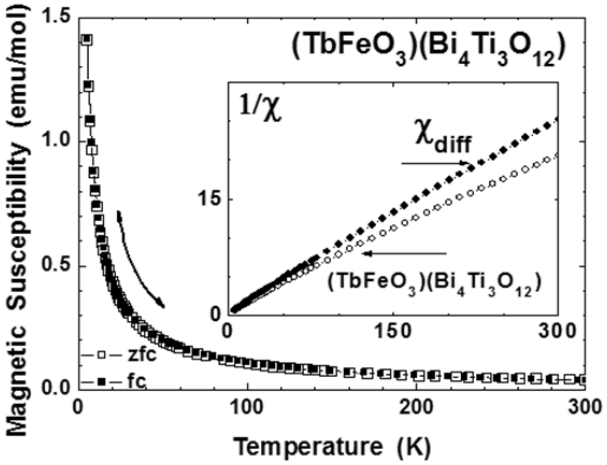

Fig. 2- Magnetic susceptibility of $TbFeBi_4Ti_3O_{15}$. Insert shows the inverse susceptibility (open circles: as measured ; filled circles: after subtraction of the $Bi_5FeTi_3O_{15}$ contribution). Susceptibilidad magnética de $TbFeBi_4Ti_3O_{15}$. El inserto muestra la inversa de la susceptibilidad (círculos abiertos: total; círculos cerrados: después de la sustracción de la contribución de $Bi_5FeTi_3O_{15}$).

3.2. Double layer series $(LnFeO_3)_2(Bi_4Ti_3O_{12})$ = $Ln_2Fe_2Bi_4Ti_3O_{18}$

Similar procedure was used for analysis of the double-layer compounds. Figure 3 shows the case of Ln = Nd, for which the contribution of the lanthanide-free component $Bi_6Fe_2Ti_3O_{18}$ amounts to about 50 % of the total signal. The thermal dependence of the calculated difference is zoomed in the insert, for temperatures going from 50 K up to 350 K. A weak maximum is observed, centered at approximately 250 K. This anomaly gets larger and moves toward higher temperatures for the gadolinium and terbium-based compounds and, for this reason, measurements were performed up to 800 K, as shown in figure 4 for the case of the terbium compound $Tb_2Fe_2Bi_4Ti_3O_{18}$. The magnetic character of this anomaly is quite evident, since it is much stronger for highly magnetic ions ($gJ(Gd^{3+}) = 7\ \mu_B$, $gJ(Tb^{3+}) = 9\ \mu_B$), it weakens for Nd ($gJ(Nd^{3+}) = 3.27\ \mu_B$) and disappears for the VanVleck Eu^{3+} ion (not shown). We exclude the possibility of a phenomenon

related to the presence of iron oxide impurities (anomaly at about 750 K) or unreacted $BiFeO_3$ (T_N = 640 K).

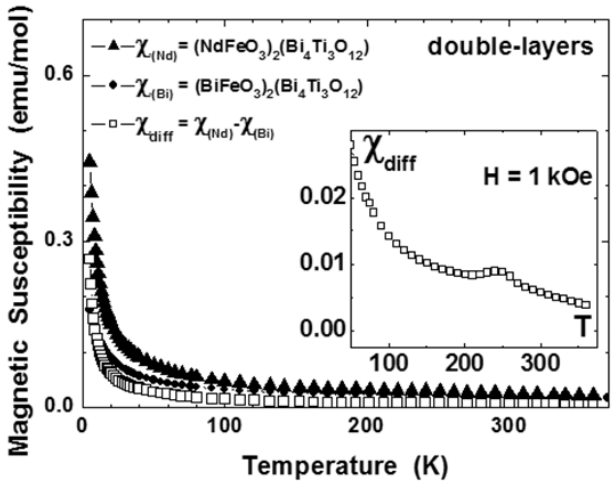

Fig. 3- Magnetic susceptibility of $Nd_2Fe_2Bi_4Ti_3O_{18}$ (filled triangles) and $Bi_6Fe_2Ti_3O_{18}$ (filled circles), and their difference χ_{diff} (open squares). The insert zooms the range [50-350K]. Susceptibilidad magnética de $Nd_2Fe_2Bi_4Ti_3O_{18}$ (triángulos llenos) y $Bi_6Fe_2Ti_3O_{18}$ (círculos llenos), y su diferencia χ_{diff} (cuadrados abiertos). El inserto muestra el rango [50-350K].

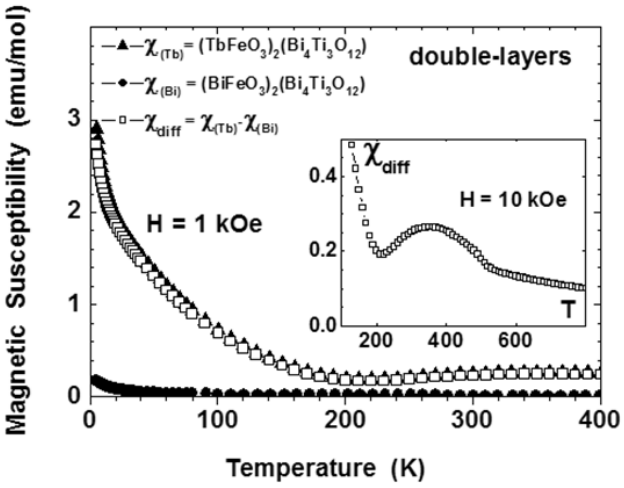

Fig. 4- Magnetic susceptibility of $Tb_2Fe_2Bi_4Ti_3O_{18}$ (filled triangles) and $Bi_6Fe_2Ti_3O_{18}$ (filled circles), and their difference χ_{diff} (open squares). The insert zooms the range [100-800K].Susceptibilidad magnética de $Tb_2Fe_2Bi_4Ti_3O_{18}$ (triángulos llenos) y $Bi_6Fe_2Ti_3O_{18}$ (círculos llenos), y su diferencia χ_{diff} (cuadrados abiertos). El inserto muestra el rango [100-800K].

The rapid increase of the magnetization below the anomaly was analyzed for Ln = Gd and Tb in terms of a Curie-Weiss law $\chi = C/(T-\Theta)$ in the range (100 K ≤ T ≤ 180 K). In both cases, the curves can be fitted by independent paramagnetic Ln^{3+} ions with large ferromagnetic exchange interactions, (i.e., $\Theta > 0$). For $(GdFeO_3)_2(Bi_4Ti_3O_{12})$, the Curie-Weiss equation was $\chi = 15.62/(T-77.6)$, which corresponds to 2 Gd ions per formula unit, of 7.90 μ_B/Gd-at and Θ = + 77.6 K, compared to an expected moment of 7.94 μ_B. In the case of $(TbFeO_3)_2(Bi_4Ti_3O_{12})$, the corresponding results were χ = 24.32/(T-80.6), due to 2 Tb ions of 9.86 μ_B/Tb-at, compared to an expected moment of 9.72 μ_B. These quite reasonable fits prompted us to subtract their contribution from the total magnetization. Figure 5 shows the experimental results before and after the subtraction of the contribution by independent Ln^{3+} ions. The broad anomaly centred at about 350 K could be reminiscent of the antiferromagnetic behaviour of the ferroic $BiFeO_3$ compound, which is a typical example of a spatially modulated antiferromagnetic spin structure with zero remanent magnetization (10-12). This means in our case that Fe^{3+}-Fe^{3+} interactions within the perovskite layers are extremely important but, at low temperatures, iron ions are coupled into a frustrated state of low remanent magnetization, just leaving the contribution of the lanthanide moment. In the absence of other examples of this series we must, however, be extremely cautious about these conclusions, especially if no such behaviour was observed in the single-layer family. More experiments (e.g., neutron diffraction) are necessary to confirm these asserts.

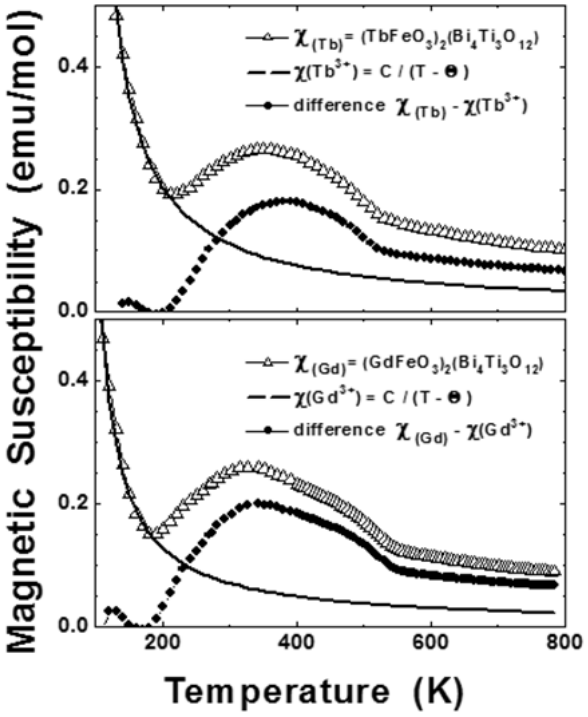

Fig. 5- Detail of the temperature dependence of the magnetic susceptibility of $Ln_2Fe_2Bi_4Ti_3O_{18}$ (Gd and Tb) : as measured (open triangles), paramagnetic contribution from independent Ln^{3+} ions (continuous line) and their difference (filled circles). Detalle de la dependencia respecto de la temperatura de la susceptibilidad magnética de $Ln_2Fe_2Bi_4Ti_3O_{18}$ (Gd and Tb): total (triángulos abiertos), contribución paramagnética de los iones independientes Ln^{3+} (línea continua), y su diferencia (círculos llenos)..

The frustrated state of the iron ions is confirmed by the magnetization curves as a function of field, measured at 5 K for all double-layer compounds (fig. 6). With the exception of Ln = Tb, for which a very slight irreversibility was observed at low field, all other samples showed fully reversible magnetization cycles, excluding long-range ferromagnetic order at these temperatures. If present, the effect of magnetic impurities is negligible in front of the large intrinsic moments of the lanthanide sublattice, and can be discarded in the present analysis.

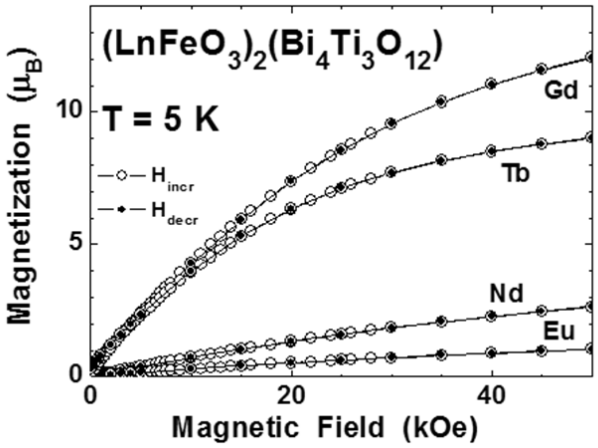

Fig. 6- Magnetization measured at 5 K for $Ln_2Fe_2Bi_4Ti_3O_{18}$ (Ln = Nd, Eu, Gd, Tb). Negligible irreversibilities were observed with increasing and decreasing fields. Magnetización medida a 5 K para $Ln_2Fe_2Bi_4Ti_3O_{18}$ (Ln = Nd, Eu, Gd, Tb). Se observaron irreversibilidades despreciables al aumentar y disminuir el campo magnético.

4. CONCLUSIONS

Magnetic properties of the lanthanide-bismuth $(LnFeO_3)_nBi_4Ti_3O_{12}$ materials strongly depend on the number n of the perovskite layers inserted in the $Bi_4Ti_3O_{12}$ structure. For single-layer compounds, a paramagnetic behaviour is observed, similar to the lanthanide-free iron-bismuth Aurivillius phase. The effective moment obtained in the case of $LnFeBi_4Ti_3O_{15}$, once the contribution of the matrix has been subtracted, corresponds to the expected value for independent non-interacting Tb^{3+} and VanVleck Eu^{3+} ions. For double-layer materials, a broad anomaly appears at high temperature, which depends on the magnetic nature of the Ln element (quite large for strongly magnetic Gd and Tb ions; weak anomaly for Nd^{3+} and negligible for Eu^{3+} moments). The origin of such anomaly, which seems related to a frustrated state of the iron ions with low remanent magnetization at low temperature, should be confirmed by other techniques, e.g. neutron diffraction, single crystals experiments, etc.

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REFERENCES

1. H.-J. Cho, W. Jo, T.W. Noh, Leakage current behaviours in rapid thermal annealed $Bi_4Ti_3O_{12}$ thin films, Appl. Phys. Lett., 65(12) 1525-1527 (1994)
2. S.B. Desu, P.C. Joshi, X. Zhang, S.O. Ryu, Thin films of layered-structure (1-x) $SrBi_2Ta_2O_9$-$xBi_3Ti(Ta_{1-y}Nb_y)O_9$ solid solution for ferroelectric random access memory devices, Appl. Phys. Lett., 71(8) 1041-1043 (1997)
3. E.C. Subbarao, A family of ferroelectric bismuth compounds, J. Phys. Chem. Solids, 23(6) 665-676 (1962)
4. O. Alvarez-Fregoso, Structural and dielectric characterization of $Sm_2Bi_2Ti_3O_{12}$ ferroelectric ceramics, J. Appl. Phys., 81(3) 1387-1391 (1997)
5. A. Srinivas, Dong-Wan Kim, Kug Sun Hong, S.V. Suryanarayana, Observation of ferroelectromagnetic nature in rare-earth-substituted bismuth iron titanate, Appl. Phys. Lett., 83(11) 2217-2219 (2003)
6. C. Moure, L. Lascano, J. Tartaj, P. Durán, Electrical behaviour of the $Bi_5FeTi_3O_{15}$ and their solid solutions with $CaBi_4Ti_4O_{15}$, Ceramics International, 29 (2003) 91-97
7. C. Moure, J. Tartaj, V. Gil, P. Durán, O. Peña, Synthesis, sintering and electrical properties of a new $LnFeBi_4Ti_3O_{15}$ compound family (Ln = Nd, Eu, Gd), IV International Conf. Inorganic Materials, Anvers (Belgium), 19-21 sept. 2004, and to be published
8. A. Srinivas, S.V. Suryanarayana, G.S. Kumar, M. Mahesh Kumar, Magnetoelectric measurements on $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$, J. Phys.: Condens. Matter 11, 3335-3340 (1999)
9. J.H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, London, 1965
10. W. Eerenstein, F.D. Morrison, J. Dho, M.G. Blamire, J.F. Scott, N.D. Mathur, Comment on Epitaxial $BiFeO_3$ multiferroic thin film hétérostructures, Science, 307, 1203a (2005)
11. J. Wang, A. Scholl, H. Zheng, S.B. Ogale, D. Viehland, D.G. Schlom, N.A. Spaldin, K.M. Rabe, M. Wuttig, L. Mohaddes, J. Neaton, U. Waghmare, T. Zhao, R. Ramesh, Response to comment on Epitaxial $BiFeO_3$ multiferroic thin film heterostructures, Science, 307, 1203b (2005)
12. H. Béa, M. Bibes, A. Barthélemy, K. Bouzehouane, E. Jacquet, A. Khodan, J.-P. Contour, S. Fusil, F. Wyczisk, A. Forget, D. Lebeugle, D. Colson, M. Viret, Influence of parasitic phases on the properties of $BiFeO_3$ epitaxial thin films, Appl. Phys. Lett., 87, 072508_1-072508_3 (2005)

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